



## Short communication

## Constructing a novel hierarchical 3D flower-like nano/micro titanium phosphate with efficient hydrogen evolution from water splitting



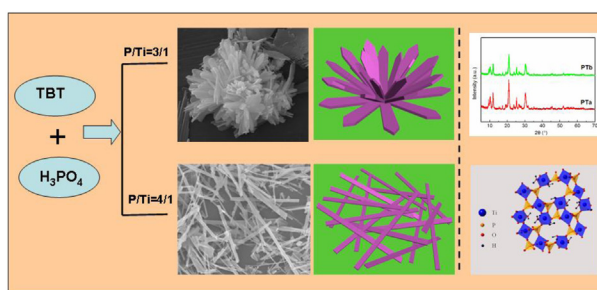
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## HIGHLIGHTS

- Shape-controlled titanium phosphate (TiP) was prepared by a one-step method.
- It is the first report of mesoporous 3D flower-like nano/micro TiP.
- The morphological change of TiP from 3D flower shape to near fibrous shape.
- Mesoporous 3D flower-like nano/micro TiP exhibited an enhanced H<sub>2</sub> productivity.

## GRAPHICAL ABSTRACT



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## ABSTRACT

A novel nano/micro hierarchical structured titanium phosphate with unique 3D flower-like morphology has been prepared by a simple hydrothermal method without adding any surfactants. The shape of the titanium phosphate could be controlled by simply adjusting the concentration of phosphoric acid. The 3D flower-like titanium phosphate with diameter of 2–3 μm is characterized by the assembly of numerous porous and connected lamella structures. Interestingly, this novel hierarchical mesoporous 3D flower-like titanium exhibits enhanced hydrogen evolution from water splitting under xenon lamp irradiation in the presence of methanol as the sacrificial reagent, which is also the first example of 3D flower-like titanium phosphate with high photocatalytic activity for water splitting. Since the use of titanium phosphate as a photocatalyst has been mostly neglected up to now, this low-cost, simple procedure and large-scale yield of 3D nano/micro structure titanium phosphate could be expected to be applicable in the synthesis of controlled, reproducible and robust photocatalytic systems.

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## 1. Introduction

Since the discovery of hydrogen evolution through the photo-electrochemical splitting of water on n-type TiO<sub>2</sub> electrodes [1], photocatalytic water splitting has been considered as one of the most important approaches to solving the world energy crisis [2–5]. However, most of the photocatalysts are not efficient for water

splitting because of their large band gap energy, poor photostability and unsuitable band positions. Many attempts have been made to improve the photocatalytic activity of these photocatalysts [6–14]. Among them, the design and controllable fabrication of nano-materials with heterostructures have become an increasingly important research area because of their large quantum yields and photoluminescence based on the quantum confinement effect [15–17].

Shape-controlled synthesis of nanocrystals is of great importance for both fundamental studies and technological applications (e.g., energy storage in electrochemical capacitors and catalysis) in

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multiple fields [18–24]. Recently, nano/micro hierarchical structured materials have garnered considerable attention since their architectures combine the features of micro- and nano-scaled materials and exhibit unique properties that differ from those of the corresponding mono-morphological structures [25–27]. These various nano/micro structures have been applied in many fields, such as lithium-ion batteries, gas sensors, dye-sensitized solar cells (DSSCs) and photocatalysts [28–31]. Moreover, phosphate-based materials have attracted the widespread attention of academia and industry because of their unique open framework structure. Among them, titanium phosphate has attracted considerable attention because of its potential to be used as an ion-exchanging reagent for cations and anions, a catalyst for the liquid-phase partial oxidation of cyclohexene by  $\text{H}_2\text{O}_2$  and for the reduction of carbon dioxide [32–36]. However, although there have been many reports on layered titanium phosphates, there are seldom reports on titanium phosphates with special shapes, especially 3D flower-like nano/micro hierarchical structured titanium phosphate. Moreover, ordered porous titanium phosphate with a relatively high surface area and shape-controlled crystalline framework is of great significance for practical applications. Titanium phosphate has considerable potential to be used as an ion-exchanging reagent or catalyst for liquid phase oxidation reactions, however, almost no attention has been paid to its photocatalytic properties, such as water splitting for  $\text{H}_2$  production.

In the present work, we report for the first time a novel mesoporous titanium phosphate with a 3D flower-like nano/micro hierarchical structure. The morphology of titanium phosphate could be changed from 3D flower-like shape to fibrous by simply varying the concentration of phosphoric acid. All the samples were tested for the photocatalytic production of  $\text{H}_2$  from water solutions under xenon lamp irradiation. Unexpectedly, it was demonstrated that the hierarchical 3D flower-like titanium phosphate results in a remarkable improvement in performance in comparison with the corresponding fibrous sample and pure sample. Therefore, the synthesis of these composites with different structures and the comparison of their catalytic activities are of great interest.

## 2. Experimental

### 2.1. Catalyst preparation

All reagents were of analytical grade and were used without further purification.

4 ml of tetrabutyl titanate (TBT) and 4 ml of acetic acid were dissolved in 20 ml of ethanol under slow stirring at room temperature, which was marked as Solution A. Then, a certain amount of  $\text{H}_3\text{PO}_4$  solution and 12 ml of diluted hydrochloric acid ( $\text{pH} = 2$ )

were mixed in 20 ml of ethanol, which was marked as Solution B. Solution B was subsequently added dropwise into solution A with vigorous stirring to form a homogeneous mixture. After stirring for 6 h, the mixture was transferred to a 100 ml Teflon-lined stainless steel autoclave and subjected to hydrothermal treatment at  $180^\circ\text{C}$  for 12 h. Finally, the powder sample was filtered, rinsed with ethanol and deionized water, and dried at  $60^\circ\text{C}$  for 12 h. The molar ratios of P to Ti were fixed at 3/1 and 4/1, which was designated as PTa and PTb respectively. Pure  $\text{TiO}_2$  was prepared by the same procedure without the addition of phosphoric acid.

### 2.2. Characterization techniques

X-ray diffraction (XRD) patterns were collected on a Rigaku D/max-2200VPC diffractometer. Scanning electron microscopy (SEM) images were performed with Nova NanoSEM 430.  $\text{N}_2$  adsorption–desorption isotherms were recorded on a Micromeritics (Norcross, GA) ASAP 2020 surface area and porosity analyzer at liquid nitrogen temperature (77 K). The specific surface area was obtained using the Brunauer–Emmett–Teller (BET) method. A Setaram Labsys (Caluire, France) thermal analyzer, the samples being heated from room temperature to  $1000^\circ\text{C}$  at  $5^\circ\text{C min}^{-1}$ .

### 2.3. $\text{H}_2$ evolution evaluation

The photocatalytic  $\text{H}_2$  evolution experiments were carried out on a LABSOLAR II photocatalytic water splitting testing system (Beijing Perfect light Technology Co., Ltd.) which consists of xenon light source, reactor, pipeline system, vacuum system, electromagnetic gas circulator and controller, sampling device and so on. After connected with the mass spectrometer, the system can realize the function of sampling and analysis online. Typically, 10 mg samples were dispersed in 100 ml of methanol solution (10 ml of methanol, 90 ml of deionized water) under magnetic stirring. A 300 W xenon lamp (PLS-SEX-300C) was employed as the light source, and the sample was irradiated vertically. Before irradiation, the system was pumped to remove air, and the amount of  $\text{H}_2$  evolved was determined using a mass spectrometer (Pfeiffer OmniStar™/ThermoStar™) connected to the photoreactor by a capillary tube.

## 3. Results and discussion

### 3.1. Crystal structure, morphology and porosity

The XRD results of the samples are shown in Fig. 1a. It is found that the XRD patterns of PTa and PTb showed the

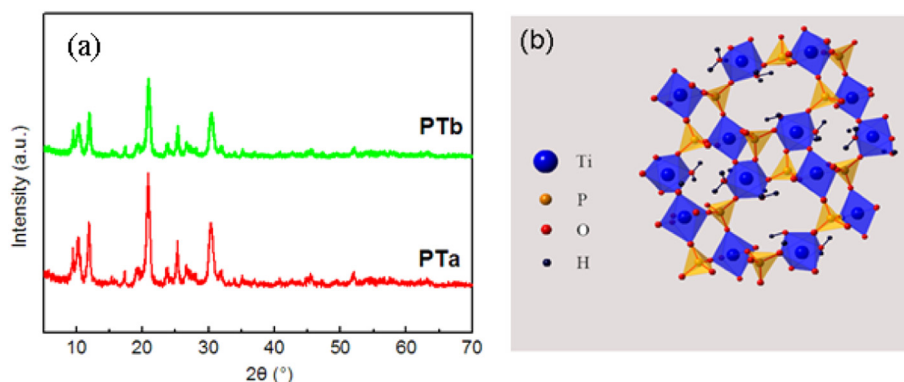
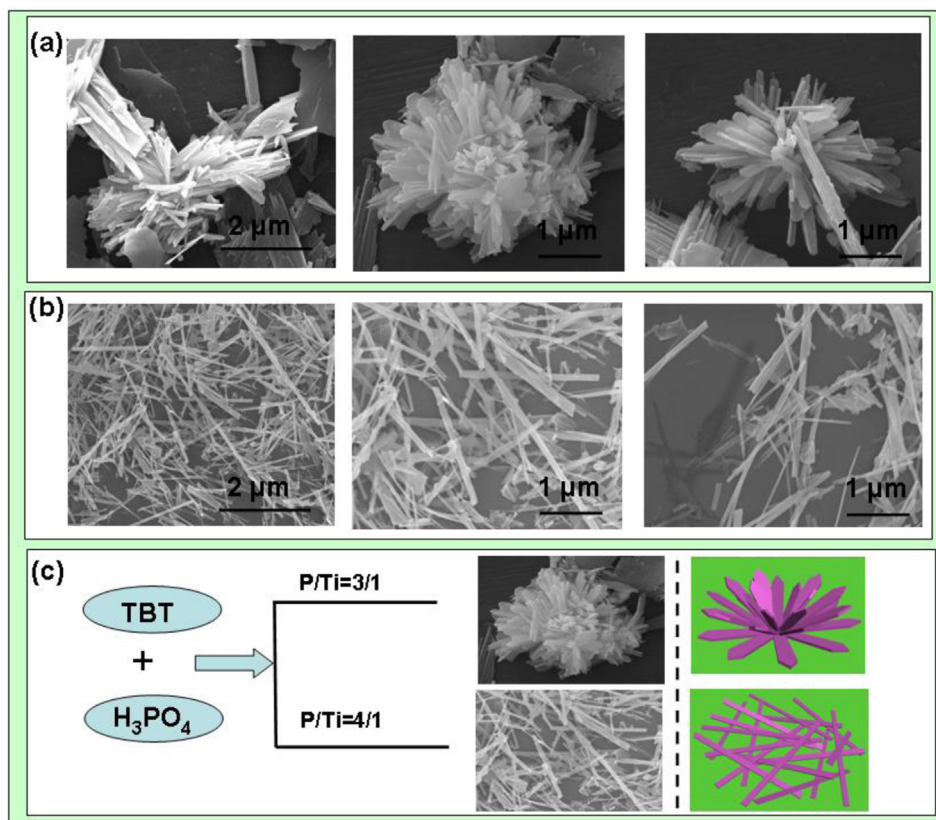


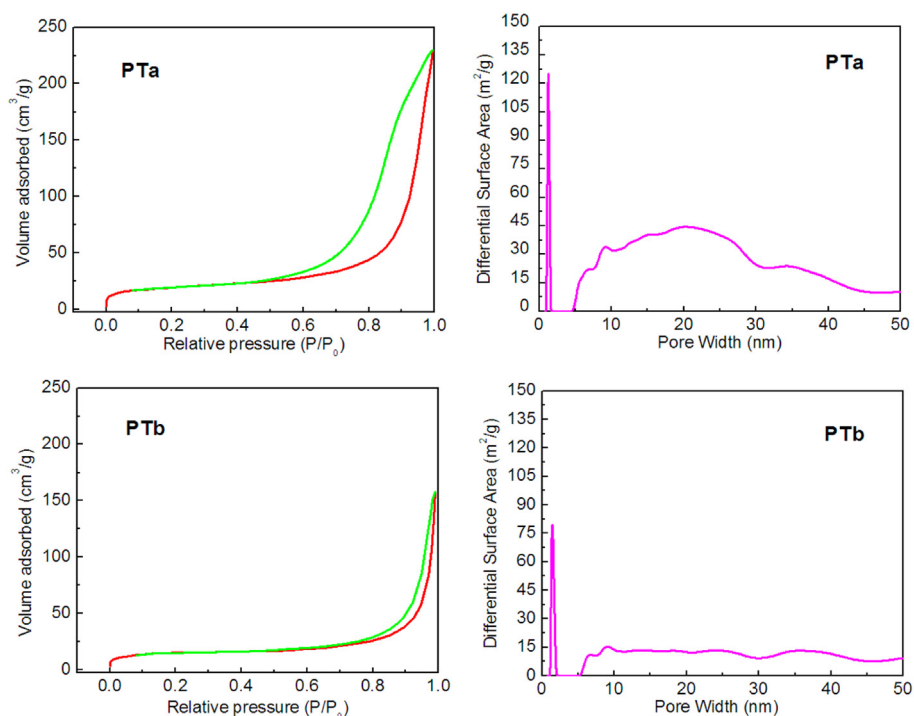
Fig. 1. (a) XRD patterns of PTa and PTb; (b) the crystal structure of  $\rho$ -titanium phosphate.



**Fig. 2.** SEM images of (a) PTa, (b) PTb and (c) schematic illustration of the preparation process for the titanium phosphate heterostructures.

characteristic peak of  $\rho$ -titanium phosphate ( $\text{Ti}_2\text{O}(\text{PO}_4)_2(\text{H}_2\text{O})_2$ , JCPDS #88-0041).  $\rho$ -titanium phosphate is crystallized in a triclinic space group, as shown in Fig. 1b, the structure consists of octahedrally coordinated Ti atoms linked by the oxygen in

the phosphate groups and in the  $\text{Ti}_2\text{O}$  group. One of the channels is formed by four Ti octahedra and four P tetrahedra. The coordinated water molecules project into the center of the channels.



**Fig. 3.**  $\text{N}_2$  adsorption–desorption isotherms and BJH pore size distribution curves (inset) of the PTa and PTb samples.

**Table 1**  
Summary of the properties of the PTa and PTb.

Samples	BET <sup>a</sup> (m <sup>2</sup> g <sup>-1</sup> )	Micro/mesoporous area <sup>b</sup> (m <sup>2</sup> g <sup>-1</sup> )	Pore size <sup>c</sup> (nm)	Pore volume <sup>d</sup> (cm <sup>3</sup> g <sup>-1</sup> )
PTa	68	21	20	0.35
PTb	50	28	22	0.28

<sup>a</sup> Determined by applying Brunauer–Emmett–Teller (BET) equation.

<sup>b</sup> T-plot micropore area.

<sup>c</sup> Adsorption average pore width (4V/A by BET).

<sup>d</sup> Single point adsorption total pore volume of pores at  $P/P_0 = 0.99$ .

Variations in the morphology and hierarchy of titanium phosphate nanostructures, including 3D flower-like nanorods and net-like nanofibers, are shown in Fig. 2. It can clearly be seen in Fig. 2a that the geometrical shapes of PTa possess a 3D flower-like nano/micro hierarchical structure composed of nanorods with a length and diameter of 2.0  $\mu\text{m}$  and 200 nm, respectively. The SEM images of the hierarchical net-like PTb nanofibers are shown in Fig. 2b. It could be observed that these randomly oriented nanofibers have a smooth and uniform surface. Their lengths could reach several micrometers, and the diameter range from 50 to 100 nm. Overall, the 3D flower-like titanium phosphate was formed when the molar ratio of P/Ti is 3/1, the fibrous titanium phosphate was formed when the molar ratio of P/Ti is 4/1, which are summarized in Fig. 2c. It can be inferred that the molar ratio of P/Ti plays an important role in determining the morphology of the samples. These characterizations demonstrate that we have successfully synthesized a novel 3D flower-like titanium phosphate titanium via a simple and facile hydrothermal method.

The nitrogen adsorption/desorption isotherms for PTa and PTb are shown in Fig. 3; these isotherms can be considered as type IV, indicating the mesoporous nature of the materials. It is clear that the  $\text{N}_2$  adsorption volume of PTa was higher than that of PTb, indicating that PTa has a larger BET surface area, which coincides with the pore size distributions found employing the Barrett–Joyner–Halenda (BJH) method. The corresponding pore size distribution shows that these materials have two pore size distributions corresponding to micropore and mesopore. The microporous distribution is mainly located at 1.5 nm, while the mesoporous distribution is located around 10–30 nm. The BET surface area, mesoporous area, pore size and pore volume are summarized in Table 1.

### 3.2. TG–DTA analysis

The differential thermal analysis (DTA) and thermal gravimetry (TG) of the PTa are shown in Fig. 4. The TG diagram shows two main steps for weight loss. The first one occurred in the range of 160–

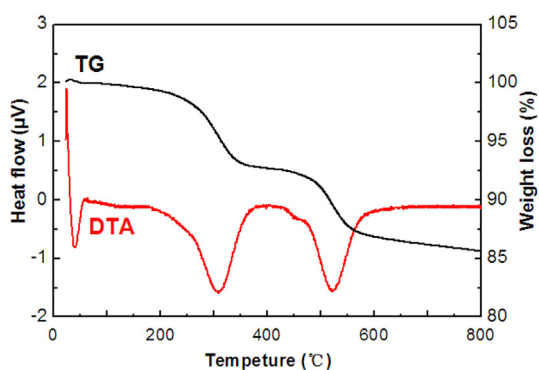


Fig. 4. TG/DTA results of the PTa samples.

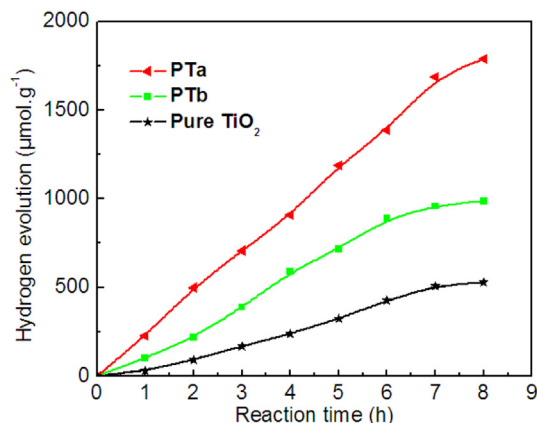


Fig. 5. Hydrogen evolution of the samples under the xenon lamp irradiation.

360 °C (weight loss was about 8% of the total weight), corresponding to the loss of chemically adsorbed water (140–310 °C). The second one, in the range of 450–600 °C (weight loss: 6%), was attributed mainly to oxy-hydroxide decompositions. The endothermic effect in the DTA curve at 50 °C was attributed to the evaporation of physically absorbed water. The endothermic peak at 310 °C was associated with the dehydration and loss of chemically adsorbed water and crystalline water, while the endothermic peak at 500 °C was attributed to oxy-hydroxides dehydroxylation. There were no significant thermal effects detected above 600 °C.

### 3.3. Photocatalytic activity

Fig. 5 shows a typical time course of  $\text{H}_2$  gas evolution for the photocatalytic decomposition of water on the prepared samples. And PTa (3D flower-like titanium phosphate) showed the highest  $\text{H}_2$  generation under xenon lamp irradiation. The  $\text{H}_2$  productivity of PTb (a hierarchical net-like titanium phosphate) was slightly inferior to that of PTa. The photocatalytic activity of pure titania is the worst. It is well-known that titania is an efficient photocatalyst in photocatalytic hydrogen production, but here the efficacy of 3D flower-like titanium phosphate in solar water splitting was much greater than that of titania. The good performance of titanium phosphate in water splitting can be explained by considering that titanium phosphate is composed of titanium and phosphate and the proportions between them can be controlled in the experimental process. Thus titanium phosphate can be envisioned as a “doped semiconductor” with the “dopant” phosphate present in well-defined structural positions. In addition, the crystal structure of the sample consists of octahedrally coordinated Ti atoms linked by the oxygen in the phosphate groups and in the  $\text{Ti}_2\text{O}$  group. One of the channels is formed by four Ti octahedra and four P tetrahedra. The twisty titanium–oxygen octahedral could be the dominant catalytic active center in solar water splitting. Moreover, the special flower-like titanium phosphate with large BET surface area provides a large reaction interface for the photocatalytic reaction, and is easy to contact more reagents and absorb more solar light irradiation, which is in favor of improving the photocatalytic hydrogen evolution.

## 4. Conclusions

In summary, shape-controlled, mesoporous, nano/micro hierarchical structured titanium phosphate with unique 3D flower-like morphology has been successfully synthesized for the first time by a facile approach without adding any surfactants. Moreover, the



drastic morphological change of the titanium phosphate from a hierarchical 3D flower-like shape to fibrous shape can be controlled by simply adjusting the concentration of phosphoric acid. And this unique nano/micro hierarchical 3D flower-like titanium phosphate also showed enhanced hydrogen evolution in photocatalytic water splitting. Thus this 3D flower-like titanium phosphate could be considered as a new powerful photocatalyst for the decomposition of pure water into H<sub>2</sub>.

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